FORM PTO-1390 (REV 10-00) U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: WAS0513PUSA

U S APPLICATION NO (If known, see 37 C F R. 1 5): 10/070843

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP00/08753	07 September 2000 (07.09.00)	09 September 1999 (09.09.99)

TITLE OF INVENTION
PROCESS FOR PREPARING ADHESIVES HAVING IMPROVED ADHESION

APPLICANT(S) FOR DO/EO/US
THOMAS KÖHLER, et al

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. X This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ___ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371
3. ___ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. X A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. X A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ___ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. X has been transmitted by the International Bureau.
   c. ___ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. X A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ___ Amendments to the claims of the International Application Under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ___ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ___ have been transmitted by the International Bureau.
   c. ___ have n t been made; however, the time limit for making such amendments has NOT expired.
   d. ___ have not been made and will not be made.
8. ___ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ___ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ___ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ___ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ___ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3 31 is included.
13. X A FIRST preliminary amendment.
    ___ A SECOND or SUBSEQUENT preliminary amendment.
14. ___ A substitute specification.
15. ___ A change of power of attorney and/or address letter
16. ___ Other items or information.

"Express Mail" Mailing Label No.: EV 011 677 680 US

Date of Deposit: 11 March 2002 (11.03.02)

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" under 37 C.F.R. 1.10 on the date indicated above and is addressed to: P.O. Box PCT, Commissioner for Patents, United States Patent and Trademark Office, Washington, D.C. 20231

Linda J. Robb

U.S. APPLICATION NO (If known, see 37 C.F.R. 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
10/070843	PCT/EP00/08753	WAS0513PUSA

17. X The following fees are submitted:

	CALCULATIONS PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO $1,040.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO $890.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO $740.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) $710.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) $100.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 890.00
Surcharge of **$130.00** for furnishing the oath or declaration later than ____ 20 ____ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$ 00.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	19 - 20 =	0	X $18.00	$ 00.00
Independent claims	1 - 3 =	0	X $84.00	$ 00.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ $280.00	$ 00.00
			TOTAL OF ABOVE CALCULATIONS =	$ 890.00
Reduction by ½ for filing by small entity. Applicant claims small entity status.				$ 00.00
			SUBTOTAL =	$ 890.00
Processing fee of **$130.00** for furnishing the English translation later than ____ 20 ____ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).			+	$ 00.00
			TOTAL NATIONAL FEE =	$ 890.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property			+	$ 00.00
			TOTAL FEES ENCLOSED =	$ 890.00
			Amount to be: refunded	$
			charged	$

a. X A check in the amount of $ 890.00 to cover the above fees is enclosed.

b. ____ Please charge my Deposit Account No. 02-3978 in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. X The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-3978. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

THOMAS KÖHLER, et al.

Group Art Unit: Unknown

Examiner: Unknown

Corresponding to PCT/EP00/08753

Filed: Herewith

For: PROCESS FOR PREPARING ADHESIVES HAVING IMPROVED ADHESION

Attorney Docket No.: WAS0513PUSA

PRELIMINARY AMENDMENT

Commissioner for Patents
United States Patent and Trademark Office
BOX PCT
Washington, D.C. 20231

Sir:

Prior to examination on the merits and prior to calculation of the filing fee, kindly amend the application as follows.

In The Specification

Please replace the Specification paragraphs as shown below. A marked up version of these changes is attached to this Amendment.

Before the paragraph beginning on page 1, prior to line 4, insert:

BACKGROUND OF THE INVENTION

1. Field of the Invention

CERTIFICATE OF MAILING UNDER 37 C.F.R. § 1.8

I hereby certify that this correspondence is being deposited with the United States Postal Service via Express Mail Label No. EV 011 677 680 US in an envelope addressed to: Commissioner for Patents, United States Patent and Trademark Office, BOX PCT, Washington, D.C. 20231 on

11 March 2002 — Date of Deposit

Linda J. Robb — Name of Person Signing

Linda J. Robb — Signature

Before the paragraph beginning on page 1, prior to line 10, insert:

2. Description of the Related Art

Please replace the paragraph beginning on page 1, at line 10, with the paragraph shown below:

Polyvinyl alcohol-stabilized vinyl acetate-ethylene copolymers in the form of their aqueous dispersions are frequently employed to bond paper and packaging materials. A disadvantage, however, is that the adhesion is often inadequate to bond to surfaces of plastic. To improve the adhesion it is common to add plasticizing additives, to modify the adhesive with polyacrylate dispersions, or to lower the glass transition temperature of the vinyl acetate-ethylene copolymer by incorporating larger amounts of ethylene into it. A disadvantage of these measures, however, is the marked reduction in the cohesion of the adhesives.

Please replace the paragraph beginning on page 1, at line 23, with the paragraph shown below:

From DE-A 19825052 it is known to improve the adhesion of adhesives based on polyvinyl alcohol-stabilized polymer dispersions by copolymerizing vinyl esters of alpha-branched, tertiary monocarboxylic acids of 11 carbon atoms.

Before the paragraph beginning on page 2, prior to line 5, insert:

SUMMARY OF THE INVENTION

Please replace the paragraph beginning on page 2, at line 5, with the paragraph shown below:

It is therefore an object of the invention to improve the adhesion of adhesives, especially those based on polyvinyl alcohol-stabilized vinyl acetate-ethylene copolymers,

without a dramatic fall in the cohesion. These and other objects are met by the post-polymerization addition of from 0.3 to 3.0 weight percent of an emulsifier to an aqueous adhesive polymer dispersion prepared by emulsion polymerization in the presence of polyvinyl alcohol.

Before the paragraph beginning on page 2, prior to line 10, insert:

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In The Claims

Kindly cancel claims 1-14 in favor of new claims 15-33.

Please add the following new claim 15-33.

15. (New) A process for the preparation of adhesives exhibiting improved adhesion, said process comprising:

a) emulsion polymerizing, in the presence of water and polyvinyl alcohol, one or more monomers selected from the group consisting of vinyl esters of optionally branched C_{1-12} carboxylic acids (meth)acrylic esters of C_{1-12} optionally branched alcohols, vinyl aromatic compounds, vinyl halides, dienes, and α-olefins to form an aqueous polymer dispersion;

b) following said step of emulsion polymerizing, adding to said aqueous polymer dispersion from 0.3% to 3.0% by weight based on the weight of the aqueous polymer dispersion of one or more emulsifiers selected from the group consisting of anionic emulsifiers, cationic emulsifiers, and non-ionic emulsifiers selected from the group consisting of alkyl polyglycol ethers, alkylaryl polyglycol ethers, polyoxyethylene-polyoxypropylene block copolymer glycols having less than 40 alkylene oxide-derived units, and mixtures thereof, to form an aqueous adhesive polymer dispersion;

c) optionally drying said aqueous adhesive polymer dispersion to form a water-redispersible adhesive powder.

16. (New) The process of claim 15, wherein said one or more monomers comprise vinyl acetate; vinyl acetate and ethylene with from 40 to 99% by weight of vinyl acetate and an ethylene content of from 1 to 60% by weight; ethylene and vinyl chloride with an ethylene content of from 1 to 40% by weight and a vinyl chloride content of from 50 to 90% by weight; vinyl acetate and further vinyl esters with from 30 to 75% by weight of vinyl acetate and from 1 to 50% by weight of one or more copolymerizable vinyl esters selected from the group consisting of vinyl laurate, vinyl pivalate, vinyl 2-ethylhexanoate, and vinyl esters of alpha-branched C_{5-11} carboxylic acids and optionally from 1 to 40% by weight of ethylene; styrene and butadiene with a styrene content of from 10 to 70% by weight; or styrene and acrylates with a styrene content of from 10 to 70% by weight; each of the above optionally in the presence of auxiliary monomers.

17. (New) The process of claim 16, wherein said auxiliary monomers are present in an amount of from 0-05 to 10.0 weight percent based on the total weight of all monomers.

18. (New) The process of claim 17, wherein said auxiliary monomers are postcrosslinking monomers, precrosslinking monomers, or mixtures thereof.

19. (New) The process of claim 18 wherein said postcrosslinking monomers are selected from the group consisting of acrylamidoglycolic acid, methacrylamidoglycolic acid methyl ester, N-methylolacrylamide, N-methylolmethacrylamide, N-methylol allylcarbamate, alkyl ethers of N-methylolacrylamide, N-methylolmethacrylamide, and mixtures thereof.

20. (New) The process of claim 18, wherein said precrosslinking monomers are selected from the group consisting of divinyl adipate, diallyl maleate, allyl methacrylate and triallyl cyanurate, and mixtures thereof.

21. (New) The process of claim 15, wherein at least one emulsifier selected from the group consisting of C_{8-18} alkyl sulfates, C_{8-18} alkyl and C_{8-18} alkylaryl ether sulfates, containing from 1 to 50 ethylene oxide units, C_{8-18} alkylsulfonates, C_{8-18} alkylarylsulfonates, diesters and monoesters of sulfosuccinic acid with monohydric alcohols or alkylphenols having 4 to 15 carbon atoms in the alkyl radical, C_{8-20} alkyl and C_{8-20} alkylaryl phosphates, C_{8-20} alkyl ether and C_{8-20} alkylaryl ether phosphates having from 1 to 50 EO units, C_{8-20} alkyl polyglycol ethers having from 5 to 40 EO units, C_{8-20} alkylaryl polyglycol ethers having from 5 to 40 EO units, is added to the aqueous dispersion after the end of the polymerization.

22. (New) The process of claim 21, wherein said at least one emulsifier is selected from the group consisting of nonylphenol ethoxylates and isotridecyl ethoxylates having from 1 to 50 ethylene oxide units, diesters and monoesters of sulfosuccinic acid with monohydric alcohols, ethoxylated alkylphenols having 4 to 15 carbon atoms in the alkyl radical, or ethoxylated alcohols are added to the aqueous dispersion after the end of the polymerization.

23. (New) The process of claim 15, wherein the amount of emulsifier added in step b) is from 0.6 to 1.5 weight percent.

24. (New) The process of claim 15, wherein polymerization is conducted in the presence of partially hydrolyzed polyvinyl alcohols containing from 75 to 95 mol% of vinyl alcohol units and having a Höppler viscosity of from 3 to 60 mPas.

25. (New) The process of claim 24, wherein the partially hydrolyzed polyvinyl alcohols containing from 75 to 95 mol% of vinyl alcohol units are used in combination with fully hydrolyzed polyvinyl alcohols having a degree of hydrolysis of greater than 95 mol% to 100 mol%.

26. (New) The process claim 15, wherein polymerization is conducted in the presence of anionic, cationic or nonionic emulsifiers.

27. (New) The process of claim 15, wherein said aqueous adhesive polymer dispersion is dried to form a water-resdispersible adhesive powder.

28. (New) In a process for adhesively bonding one or more substrates together, the improvement comprising bonding said one or more substrates with an adhesive of claim 15.

29. (New) The process of claim 28 wherein said process of adhesively bonding comprises bonding paper, packaging materials, or book binding.

30. (New) The process of claim 28 wherein said one or more substrates comprises wood.

31. (New) The process of claim 30 wherein said substrate comprises parquet.

32. (New) The process of claim 28 wherein at least one of said one or more substrates comprises fiber materials.

33. The process of claim 28 wherein said substrate comprises tile.

Remarks

Claims 15-33 are pending. Early favorable consideration is respectfully requested. The claims have been amended to reflect U.S. practice, and to eliminate multiple dependencies. No new matter has been added by virtue of these amendments. Early favorable consideration is respectfully requested.

Respectfully submitted,

THOMAS KÖHLER, et al.

By _____

William G. Conger
Reg. No. 31,209
Attorney/Agent for Applicant

Date: March 11, 2002

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Attachment

VERSION WITH MARKINGS TO SHOW CHANGES MADE

Before the paragraph beginning on page 1, prior to line 4, insert:

BACKGROUND OF THE INVENTION

1. Field of the Invention

Before the paragraph beginning on page 1, prior to line 10, insert:

2. Description of the Related Art

Please replace the paragraph beginning on page 1, at line 10, with the paragraph shown below:

Polyvinyl alcohol-stabilized vinyl acetate-ethylene copolymers in the form of their aqueous dispersions are frequently employed to bond paper and packaging materials. A disadvantage, however, is that the adhesion is often inadequate to bond to surfaces of plastic. To improve the adhesion it is common to add plasticizing additives, to modify the adhesive with polyacrylate dispersions, or to lower the glass transition temperature of the vinyl acetate-ethylene copolymer by incorporating larger amounts of ethylene into it. A disadvantage of these measures, however, is the marked reduction in the cohesion of the adhesives.

Please replace the paragraph beginning on page 1, at line 23, with the paragraph shown below:

From DE-A 19825052 it is known to improve the adhesion of adhesives based on polyvinyl alcohol-stabilized polymer dispersions by copolymerizing vinyl esters of alpha-branched, tertiary monocarboxylic acids of 11 carbon atoms.

Before the paragraph beginning on page 2, prior to line 5, insert:

SUMMARY OF THE INVENTION

Please replace the paragraph beginning on page 2, at line 5, with the paragraph shown below:

It is therefore an object of the invention to improve the adhesion of adhesives, especially those based on polyvinyl alcohol-stabilized vinyl acetate-ethylene copolymers, without a dramatic fall in the cohesion. These and other objects are met by the post-polymerization addition of from 0.3 to 3.0 weight percent of an emulsifier to an aqueous adhesive polymer dispersion prepared by emulsion polymerization in the presence of polyvinyl alcohol.

Before the paragraph beginning on page 2, prior to line 10, insert:

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Process for preparing adhesives having improved adhesion

The invention relates to a process for preparing adhesives having improved adhesion and to the use of the adhesives obtainable by this process in adhesive compositions for paper, packaging, wood and textiles and in construction adhesives.

Polyvinyl alcohol-stabilized vinyl acetate-ethylene copolymers in the form of their aqueous dispersions are frequently employed to bond paper and packaging materials. A disadvantage, however, is that the adhesion is often inadequate to bond to surfaces of plastic. To improve the adhesion it is common to add plasticizing additives, to modify the adhesive with polyacrylate dispersion, or to lower the glass transition temperature of the vinyl acetate-ethylene copolymer by incorporating larger amounts of ethylene into it. A disadvantage of these measures, however, is the marked reduction in the cohesion of the adhesives.

From DE-A 19825052 it is known to improve the adhesion of adhesives based on polyvinyl alcohol-stabilized polymer dispersion by copolymerizing vinyl esters of alpha-branched, tertiary monocarboxylic acids of 11 carbon atoms.

EP-A 385734 proposes improving the adhesion to nonpolar substances by using adhesives based on vinyl acetate-ethylene copolymer dispersions prepared in the presence of a defined amount of partially hydrolyzed polyvinyl alcohol and of a nonionic polyoxyethylene of defined HLB. A disadvantage is that only a slight improvement in the adhesion is achieved, with poorer heat stability.

JP-A 95/068504 describes adhesives containing from 14 to 30% by weight of nonionic emulsifier, based on the polymer fraction of an aqueous polymer dispersion. The

serious disadvantage of this approach is that, with the large amounts of added emulsifier, the setting and heat stability are drastically impaired.

It is therefore an object of the invention to improve the adhesion of adhesives, especially those based on polyvinyl alcohol-stabilized vinyl acetate-ethylene copolymers, without a dramatic fall in the cohesion.

The invention provides a process for preparing adhesives having improved adhesion, in the form of their aqueous dispersions or water-redispersible dispersion powders, by emulsion polymerization of one or more monomers from the group consisting of the vinyl esters of unbranched and branched carboxylic acids of 1 to 12 carbon atoms, the esters of acrylic acid and methacrylic acid with branched and unbranched alcohols of 1 to 12 carbon atoms, vinylaromatic compounds, vinyl halides, dienes and alpha-olefins in the presence of polyvinyl alcohol and, where appropriate, drying of the dispersion thus obtainable, characterized in that, after the end of the polymerization, from 0.3 to 3.0% by weight, based on the overall weight of the dispersion, of one or more emulsifiers from the group consisting of anionic, cationic and nonionic emulsifiers, with the exception of polyalkylene oxides, are added to the dispersion.

Preferred vinyl esters are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl 2-ethylhexanoate, vinyl laurate, 1-methylvinyl acetate, vinyl pivalate, and vinyl esters of alpha-branched monocarboxylic acids of 5 to 11 carbon atoms, such as VeoVa9, VeoVa10 (trade names of Shell). Vinyl acetate is particularly preferred.

Preferred methacrylates or acrylates are methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, n-butyl acrylate, t-butyl acrylate, n-butyl methacrylate, t-butyl

methacrylate, and 2-ethylhexyl acrylate. Methyl acrylate, methyl methacrylate, n-butyl acrylate and 2-ethylhexyl acrylate are particularly preferred.

Preferred dienes are 1,3-butadiene and isoprene. Preferred olefins are ethene and propene. Preferred vinylaromatic compounds are styrene, methylstyrene, and vinyltoluene, especially styrene. A preferred vinyl halide is vinyl chloride.

If desired it is also possible to copolymerize from 0.05 to 10.0% by weight, based on the overall weight of the monomers, of auxiliary monomers from the group consisting of ethylenically unsaturated mono- and dicarboxylic acids and their amides, such as acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, acrylamide, and methacrylamide; ethylenically unsaturated sulfonic acids and their salts, preferably vinylsulfonic acid and 2-acrylamidopropanesulfonate, and N-vinylpyrrolidone.

Further examples of auxiliary monomers in the stated amounts are postcrosslinking comonomers such as acrylamidoglycolic acid (AGA), methacrylamidoglycolic acid methyl ester (MAGME), N-methylolacrylamide (NMA), N-methylolmethacrylamide (NMMA), N-methylol allylcarbamate, alkyl ethers of N-methylolacrylamide or N-methylolmethacrylamide such as the isobutoxy ethers or n-butoxy ethers thereof. Further examples are precrosslinking comonomers such as polyethylenically unsaturated comonomers, examples including divinyl adipate, diallyl maleate, allyl methacrylate or triallyl cyanurate. It is preferred to use the crosslinking comonomers in an amount of from 0.1 to 3.0% by weight, based on the overall weight of the comonomers.

Further examples of auxiliary monomers in the stated amounts are hydrophobicizing and incipiently crosslinking alkoxysilane-functional monomers such as

acryloxypropyltri(alkoxy)silanes and methacryloxypropyltri(alkoxy)silanes, vinyltrialkoxysilanes and vinylmethyldialkoxysilanes, the alkoxy groups present possibly being, for example, methoxy, ethoxy, methoxyethylene, ethoxyethylene, methoxypropylene glycol ether and ethoxypropylene glycol ether radicals. Preference is given to vinyltriethoxysilane and gamma-methacryloxypropyltriethoxysilane.

The polymer composition is generally chosen so as to give a glass transition temperature Tg of from -30°C to +40°C. The glass transition temperature Tg of the polymers can be determined in a known manner by means of Differential Scanning Calorimetry (DSC). The Tg can also be calculated approximately in advance by means of the Fox equation. According to Fox T. G., Bull. Am. Physics Soc. 1, 3, page 123 (1956), it holds true that: $1/Tg = x_1/Tg_1 + x_2/Tg_2 + \ldots + x_n/Tg_n$, where x_n is the mass fraction (% by weight/100) of the monomer n and Tg_n is the glass transition temperature in degrees Kelvin of the homopolymer of the monomer n. Tg values for homopolymers are listed in Polymer Handbook 3rd Edition, J. Wiley & Sons, New York (1989).

Preferred monomer compositions comprise:
vinyl acetate, or
vinyl acetate and ethylene with from 40 to 99% by weight of vinyl acetate and an ethylene content of from 1 to 60% by weight; or
ethylene and vinyl chloride with an ethylene content of from 1 to 40% by weight and a vinyl chloride content of from 50 to 90% by weight; or
vinyl acetate and further vinyl esters with from 30 to 75% by weight of vinyl acetate and from 1 to 50% by weight of one or more copolymerizable vinyl esters from the group consisting of vinyl laurate, vinyl pivalate, vinyl 2-ethylhexanoate, and vinyl esters of an alpha-branched carboxylic acid of 5 to 11 carbon atoms, with or without from 1 to 40% by weight of ethylene in addition;

or
vinyl acetate and acrylates with from 30 to 90% by weight of vinyl acetate and from 1 to 60% by weight of acrylate, especially n-butyl acrylate or 2-ethylhexyl acrylate, with or without from 1 to 40% by weight of ethylene in addition; or
n-butyl acrylate or 2-ethylhexyl acrylate; or
methyl methacrylate and n-butyl acrylate and/or 2-ethylhexyl acrylate; or
vinyl chloride and acrylates, especially n-butyl acrylate or 2-ethylhexyl acrylate; or
styrene and butadiene with a styrene content of from 10 to 70% by weight; or
styrene and acrylates such as n-butyl acrylate or 2-ethylhexyl acrylate with a styrene content of in each case from 10 to 70% by weight.

The percentages by weight above add up, together where appropriate with the proportion of the stated auxiliary monomers, to 100% by weight.

Maximum preference is given to the copolymerization of vinyl acetate and ethylene with from 40 to 99% by weight vinyl acetate and an ethylene content of from 1 to 60% by weight, it being possible, if desired, for one or more of the stated auxiliary monomers to be copolymerized as well.

Suitable emulsifiers are anionic, cationic or nonionic emulsifiers or mixtures thereof, for example:
1) Alkyl sulfates, particularly those having an alkyl chain length of 8 to 18 carbon atoms, alkyl and alkylaryl ether sulfates having 8 to 18 carbon atoms in the hydrophobic radical and from 1 to 50 ethylene oxide units.
2) Sulfonates, especially alkylsulfonates of 8 to 18 carbon atoms, alkylarylsulfonates of 8 to 18 carbon atoms, esters and monoesters of sulfosuccinic acid with

monohydric alcohols or alkylphenols having 4 to 15 carbon atoms in the alkyl radical; if desired, these alcohols or alkylphenols may also be ethoxylated with from 1 to 40 ethylene oxide units.

3) Phosphoric acid partial esters and their alkali metal salts and ammonium salts, especially alkyl and alkylaryl phosphates having 8 to 20 carbon atoms in the organic radical, alkyl ether and alkylaryl ether phosphates having 8 to 20 carbon atoms in the alkyl or alkylaryl radical and from 1 to 50 EO units.

4) Alkyl polyglycol ethers preferably having from 5 to 40 EO units and alkyl radicals of 8 to 20 carbon atoms.

5) Alkylaryl polyglycol ethers preferably having from 5 to 40 EO units and 8 to 20 carbon atoms in the alkyl and aryl radicals.

6) Ethylene oxide/propylene oxide (EO/PO) block copolymers preferably having from 5 to 40 EO and/or PO units.

Preference is given to alkyl polyglycol ethers, with particular preference having from 5 to 40 EO units and alkyl radicals of 8 to 20 carbon atoms, alkylaryl polyglycol ethers, with particular preference having from 5 to 40 EO units and 8 to 20 carbon atoms in the alkyl and aryl radicals, such as nonylphenol ethoxylates and isotridecyl ethoxylates having from 1 to 50 ethylene oxide units. Likewise preferred are esters and monoesters of sulfosuccinic acid with monohydric alcohols, alkylphenols having 4 to 15 carbon atoms in the alkyl radical, or ethoxylated alcohols.

The preparation, in accordance with the emulsion polymerization process, is conducted in conventional reactors or pressure reactors in a temperature range from 30°C to 120°C and is initiated by the methods commonly employed for emulsion polymerization. In the case of the copolymerization of gaseous monomers such as ethylene it

is preferred to operate at a pressure of from 5 to 85 $bar_{(abs.)}$. Initiation is effected by means of the customary, at least partially water-soluble free-radical initiators, which are employed preferably in amounts of from 0.01 to 3.0% by weight based on the overall weight of the monomers. Examples of such initiators are potassium persulfate, sodium persulfate, hydrogen peroxide, t-butyl peroxide, t-butyl hydroperoxide; potassium peroxodiphosphate, and azobisisobutyronitrile. If desired, said free-radical initiators can also be combined, in a known manner, with from 0.01 to 0.5% by weight, based on the overall weight of the monomers, of reducing agents. Suitable examples are alkali metal formaldehyde-sulfoxylates and acorbic acid, and isoascorbic acid. In the case of redox initiation it is preferred to meter in one or both redox catalyst components during the polymerization.

The polymerization takes place in the presence of polyvinyl alcohol as a protective colloid, generally in an amount of from 0.1 to 15% by weight, preferably from 1 to 10% by weight, based on the overall weight of the monomers. Preference is given to partially hydrolyzed polyvinyl alcohols containing from 75 to 95 mol%, of vinyl alcohol units and having a Höppler viscosity of from 3 to 60 mPas (4% strength aqueous solution, Höppler method in accordance with DIN 53015), where appropriate in combination with fully hydrolyzed polyvinyl alcohols having a degree of hydrolysis of more than 95 mol%, preferably from 98 to 100 mol%.

The polymerization is preferably conducted without emulsifier. Alternatively, it is possible during the polymerization to employ any of the emulsifiers commonly used for emulsion polymerization. Suitable emulsifiers include the abovementioned anionic, cationic and nonionic emulsifiers, in their customary amounts of from 0.1 to 6% by weight, based on the overall weight of the monomers. The desired pH range for the polymerization, which

generally lies between 2.5 and 10, preferably between 3 and 8, can be set in a known manner by means of acids, bases and customary buffer salts, such as alkali metal phosphates or alkali metal carbonates. In order to adjust the molecular weight it is possible to add the commonly employed regulators in the polymerization, examples being mercaptans, aldehydes and chlorinated hydrocarbons.

Irrespective of the chosen polymerization process, the polymerization can be conducted batchwise or continuously, with or without the use of seed latices, with an initial charge comprising some or all of the constituents of the reaction mixture, or with an initial charge comprising a portion of some or all of the constituents of the reaction mixture, with the remaining portion(s) being metered in subsequently, or by the metering process without an initial charge. The solids content of the dispersion obtainable in this way is from 20 to 75%.

After the end of the polymerization, from 0.3 to 3.0% by weight, preferably from 0.6 to 1.5% by weight, based in each case on the overall weight of the dispersion, of one or more emulsifiers from the group of the abovementioned anionic, cationic and nonionic emulsifiers are added.

In order to prepare adhesives in powder form, the emulsifier-modified aqueous dispersion may be subsequently dried. The dispersion can be dried by means of spray drying, freeze drying or fluidized-bed drying. Preference is given to spray drying in customary spray drying plants, in which atomization can be effected by means of single-, dual- or multi-fluid nozzles or with a rotating disk. The exit temperature is generally chosen to be in the range from 55°C to 100°C, preferably from 65°C to 90°C, depending on the plant, on the Tg of the resin and on the desired degree of drying.

For spray drying, the dispersion of the polymer, with a solids content of preferably from 20% to 75%, is sprayed together with protective colloids as an atomization aid and dried. Examples of protective colloids which can be employed in this procedure are partially hydrolyzed polyvinyl alcohols, polyvinylpyrrolidones, starches, melamineformaldehydesulfonates, and naphthaleneformaldehydesulfonates. In this process step it is preferred to add from 5 to 20% by weight of protective colloid, based on the polymer. If desired, additives may also be added to the polymer powder. Examples of modifying additives are antiblocking agents, dyes, pigments, plasticizers, film-forming auxiliaries, antifoams, catalysts, rheological assistants, thickeners, and tackifiers.

The aqueous dispersions and water-redispersible redispersion powders of the invention are suitable as adhesives for bonding various substrates: for example, wood, cardboard, paper and fiber materials. The dispersions and powders are particularly useful as paper adhesives, packaging adhesives, bookbinding adhesives, wood adhesives, parquet adhesives, as adhesives for fiber materials and as adhesives in the construction sector, examples being tile adhesives.

For these applications the dispersions and/or powders can be modified with the appropriate additives. Suitable additives include fillers such as chalk or gypsum. It is also possible to add wetting agents, dispersants, thickeners, defoamers and/or preservatives.

A surprising feature is the improved adhesion of the adhesive raw materials to a variety of substrates, which is observed even when very small amounts of emulsifiers are added subsequently. Where the emulsifiers are actually added during the polymerization of the polymer dispersion, this effect of improving adhesion occurs to

a far lesser extent, and there are marked decreases in setting rate and cohesion. At amounts above 1.5% by weight of emulsifier, based on dispersion, the increase in adhesion is admittedly obtained, but setting rate and cohesion decrease as compared with the unmodified dispersion.

The examples which follow serve to illustrate the invention:

Preparation of the adhesive dispersions:

A pressure reactor was charged with 5 parts by weight of a partially hydrolyzed polyvinyl alcohol having a degree of hydrolysis of 90 mol%, 104 parts by weight of water and 100 parts by weight of vinyl acetate. This initial charge was heated to 50°C, and ethylene was injected with a pressure of 50 bar. After the temperature had reached equilibrium, a solution of 0.2 part by weight of potassium persulfate in 5.8 parts by weight of water and a solution of 0.1 part by weight of ascorbic acid in 5.8 parts by weight of water were metered in. Once at an end, polymerization resulted in a dispersion having a solids content of 55% and a copolymer composition of 18% by weight ethylene and 82% by weight vinyl acetate.

The adhesives for examples 2 to 10, and the comparative examples 11 and 15, were prepared by subsequent addition of emulsifier of the type and in the amount indicated in table 1 (% by weight emulsifier based on overall weight of the polymer dispersion).

For the adhesives of comparative examples 12 to 14, the stated emulsifiers were added in the stated amount actually during the polymerization.

In comparative example 1, emulsifier was added neither during nor after the polymerization.

The adhesives were tested using the following test methods:

Determination of the total adhesion (TA):

Paper test strips (10 × 50 mm) were coated with a 50 µm coat of each of the test adhesives and were bonded to seven different plastic films. After a drying time of 2 hours the test strips were peeled off and, in the course of this procedure, the bond strength was assessed as follows:

1 = very good adhesion, 100% tearout of material
2 = good adhesion, predominantly tearout of material
3 = adhesion, separation with resistance without tearout of material
4 = no adhesion, flaking

The 7 assessment values were added to give the total adhesion.

Determination of the setting rate (SR):

During the setting process of a dispersion adhesive there is an increase in the strength of the bond. The setting process can be described by the change in the strength of a bonded joint as a function of time. This was done by measuring the time at which a bonded area of 1 cm^2 just withstood an acceleration-free load of 2 N perpendicular to the bond plane. The test procedure was repeated until the shortest setting time had been narrowed down to ± 0.2 seconds.

Determination of the heat stability (cohesion, HS):

6 test specimens were produced each with a bonded area of 9 cm^2. This was done by providing two plywood rods (125 mm × 30 mm × 4 mm) in each case with a coating of adhesive in a thickness of 100 µm over a length of 30 mm, storing these rods in a closed press for 1 minute without pressure and then for 30 minutes with a pressure of

0.2 N/mm^2. The test specimens were subsequently stored for 7 days at 23°C and 50% atmospheric humidity and before testing were conditioned at 70 ± 0.5°C in a circulating-air drying cabinet for 4 hours. Following storage, the bond strength of the test specimens was determined in the tensile shear test, in which a tensile tester machine pulled the bonded test specimens apart at a rate of 50 mm/min until they fractured. The maximum force F_{Max} occurring at the time of fracture was measured. The bond strength T is calculated from $T = F_{Max}/A$, where A is the bonded test area in mm^2.

The test results are compiled in Table 1:

Comparison of the results of example 2 to 6 with that of comparative example 1 shows that even with small amounts and subsequent addition of emulsifier a marked improvement is achieved in the adhesion (TA) while at the same time there is at most a slight reduction in the cohesion (HS).

This effect becomes particularly marked when using amounts of from 0.6% by weight to 1.5% by weight (examples 2-6, 8, 9), with an optimum being obtained in respect of adhesion (TA), setting rate (SR) and cohesion (HS).

Below 0.6% by weight (example 7), no significant increase in adhesion is obtained.

With added amounts of more than 3.0% by weight (comparative example 11, 15), the adhesion is, admittedly, still improved, but with a markedly increased setting rate (SR) and a dramatic fall in cohesion (comp. ex. 15).

Comparison of example 2 with comparative example 14 shows that the improvement in adhesion occurs only when the emulsifier is added subsequently.

Table 1:

Example	Emulsifier	TA	SR	HS
Comp. Ex. 1	---	22	2.2	2.4
Ex. 2	1.0% emulsifier 1	16	2.2	2.3
Ex. 3	1.0% emulsifier 2	19	3.4	2.1
Ex. 4	1.0% emulsifier 3	16	2.6	2.0
Ex. 5	1.0% emulsifier 4	17	4.4	2.2
Ex. 6	1.0% emulsifier 5	16	2.0	2.3
Ex. 7	0.3% emulsifier 1	22	2.2	2.4
Ex. 8	0.6% emulsifier 1	21	2.2	2.3
Ex. 9	1.5% emulsifier 1	16	2.6	2.2
Ex. 10	3.0% emulsifier 1	15	4.4	2.2
Comp. Ex. 11	5.0% emulsifier 1	15	4.8	2.2
Comp. Ex. 12	0.5% emulsifier 2 copol.	22	1.8	2.0
Comp. Ex. 13	0.5% emulsifier 1 copol.	20	2.0	2.2
Comp. Ex. 14	1.0% emulsifier 1 copol.	20	2.1	2.0
Comp. Ex. 15	15% emulfisier 1	7	16.1	1.1
Comp. Ex. 16	1.0% plasticizer	20	2.0	2.4

% = addition of emulsifier in % solids based on aqueous dispersion;

TA = total adhesion, SR = setting rate in sec, HS = heat stability (cohesion) in N/mm^2.

Emulsifier 1 = isotridecyl ethoxylate with 15 ethylene oxide units (Genapol X 150)

Emulsifier 2 = isotridecyl ethoxylate with 36 ethylene

oxide units (Genapol X 360)

Emulsifier 3 = sulfosuccinate monoester with ethoxylated alcohol (Aerosol A 102)

Emulsifier 4 = diisohexyl sulfosuccinate (aerosol MA)

Plasticizer = dibutyl adipate (DBA)

Emulsifier 5 = isotridecyl ethoxylate with 5 ethylene oxide units (Genapol X 50)

Patent claims:

1. A process for preparing adhesives having improved adhesion, in the form of their aqueous dispersions or water-redispersible dispersion powders, by emulsion polymerization of one or more monomers from the group consisting of the vinyl esters of unbranched and branched carboxylic acids of 1 to 12 carbon atoms, the esters of acrylic acid and methacrylic acid with branched and unbranched alcohols of 1 to 12 carbon atoms, vinylaromatic compounds, vinyl halides, dienes and alpha-olefins in the presence of polyvinyl alcohol and, where appropriate, drying of the dispersion thus obtainable, characterized in that, after the end of the polymerization, from 0.3 to 3.0% by weight, based on the overall weight of the dispersion, of one or more emulsifiers from the group consisting of anionic, cationic and nonionic emulsifiers are added to the dispersion.

2. The process as claimed in claim 1, characterized in that monomers polymerized comprise compositions with vinyl acetate; or vinyl acetate and ethylene with from 40 to 99% by weight of vinyl acetate and an ethylene content of from 1 to 60% by weight; or ethylene and vinyl chloride with an ethylene content of from 1 to 40% by weight and a vinyl chloride content of from 50 to 90% by weight; or vinyl acetate and further vinyl esters with from 30 to 75% by weight of vinyl acetate and from 1 to 50% by weight of one or more copolymerizable vinyl esters from the group consisting of vinyl laurate, vinyl pivalate, vinyl 2-ethylhexanoate, and vinyl esters of an alpha-branched carboxylic acid of 5 to 11 carbon atoms, with or without from 1 to 40% by weight of ethylene in addition; or styrene and butadiene with a styrene content of from 10 to 70% by weight; or styrene and acrylates with a styrene content of in each case from 10 to 70% by weight; in the presence if desired of auxiliary monomers.

3. The process as claimed in claim 2, characterized in that auxiliary monomers copolymerized comprise postcrosslinking comonomers such as acrylamidoglycolic acid, methacrylamidoglycolic acid methyl ester, N-methylolacrylamide, N-methylolmethacrylamide, N-methylol allylcarbamate, alkyl ethers of N-methylolacrylamide, N-methylolmethacrylamide and/or precrosslinking, polyethylenically unsaturated comonomers such as divinyl adipate, diallyl maleate, allyl methacrylate and triallyl cyanurate in an amount of from 0.05 to 10.0% by weight, based on the overall weight of the monomers.

4. The process as claimed in claims 1 to 3, characterized in that, as emulsifiers, one or more from the group consisting of alkyl sulfates of 8 to 18 carbon atoms, alkyl and alkylaryl ether sulfates of 8 to 18 carbon atoms in the hydrophobic radical and from 1 to 50 ethylene oxide units, alkylsulfonates of 8 to 18 carbon atoms, alkylarylsulfonates of 8 to 18 carbon atoms, esters and monoesters of sulfosuccinic acid with monohydric alcohols or alkylphenols having 4 to 15 carbon atoms in the alkyl radical, alkyl and alkylaryl phosphates having 8 to 20 carbon atoms in the organic radical, alkyl ether and alkylaryl ether phosphates having 8 to 20 carbon atoms in the alkyl or alkylaryl radical and from 1 to 50 EO units, alkyl polyglycol ethers preferably having from 5 to 40 EO units and alkyl radicals of 8 to 20 carbon atoms, alkylaryl polyglycol ethers having from 5 to 40 EO units and 8 to 20 carbon atoms in the alkyl and aryl radicals, ethylene oxide/propylene oxide (EO/PO) block copolymers having from 5 to 40 EO and/or PO units are added to the aqueous dispersion after the end of the polymerization.

5. The process as claimed in claim 4, characterized in that, as emulsifiers, nonylphenol ethoxylates and isotridecyl ethoxylates having from 1 to 50 ethylene oxide units, esters and monoesters of sulfosuccinic acid with monohydric alcohols, alkylphenols having 4 to 15

carbon atoms in the alkyl radical or ethoxylated alcohols are added to the aqueous dispersion after the end of the polymerization.

6. The process as claimed in claim 1 to 5, characterized in that after the end of the polymerization from 0.6 to 1.5% by weight, based on the overall weight of the dispersion, of emulsifier are added to the dispersion.

7. The process as claimed in claim 1 to 6, characterized in that polymerization is conducted in the presence of partially hydrolyzed polyvinyl alcohols containing from 75 to 95 mol% of vinyl alcohol units and having a Höppler viscosity of from 3 to 60 mPas.

8. The process as claimed in claim 7, characterized in that the partially hydrolyzed polyvinyl alcohols containing from 75 to 95 mol% of vinyl alcohol units are used in combination with fully hydrolyzed polyvinyl alcohols having a degree of hydrolysis of greater than 95 mol% to 100 mol%.

9. The process as claimed in claim 1 to 8, characterized in that the polymerization is conducted in the presence of anionic, cationic or nonionic emulsifiers.

10. The process as claimed in claim 1 to 9, characterized in that, in order to prepare adhesives in powder form, the emulsifier-modified aqueous dispersion is dried.

11. The use of the process products as claimed in claim 1 to 10 as paper adhesives, packaging adhesives and bookbinding adhesives.

12. The use of the process products as claimed in claim 1 to 10 as wood adhesives, especially parquet adhesives.

13. The use of the process products as claimed in claim 1 to 10 as adhesives for fiber materials.

14. The use of the process products as claimed in claim 1 to 10 as adhesives in the construction sector, especially tile adhesives.

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— *Vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen.*

Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: METHOD FOR PRODUCING ADHESIVES HAVING IMPROVED ADHESION

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON KLEBEMITTELN MIT VERBESSERTER ADHÄSION

(57) **Abstract:** The invention relates to a method for producing adhesives having improved adhesion in the form of their aqueous dispersions or dispersion powder that can be redispersed in water. Said adhesives are produced by carrying out the emulsion polymerization of one or more monomers selected from the group of the vinyl esters of unbranched and branched carboxylic acids having 1 to 12 C atoms, of the esters of acrylic acid and methacrylic acid with branched and unbranched alcohols having 1 to 12 C atoms, of vinyl aromatic compounds, vinyl halides, dienes and alpha olefins. The emulsion polymerization is carried out in the presence of polyvinyl alcohol and the dispersion obtained thereby is optionally dried. The inventive method is characterized in that after completion of the polymerization, one or more emulsifiers selected from the group of the anionic, cationic and non-ionic emulsifiers is/are added to the dispersion in the amount of 0.3 to 3.0 wt. % with regard to the total weight of the dispersion.

(57) **Zusammenfassung:** Gegenstand der Erfindung ist ein Verfahren zur Herstellung von Klebemitteln mit verbesserter Adhäsion, in Form deren wässrigen Dispersionen oder in Wasser redispergierbaren Dispersionspulver, durch Emulsionspolymerisation von einem oder mehreren Monomeren aus der Gruppe der Vinylester von unverzweigten und verzweigten Carbonsäuren mit 1 bis 12 C-Atomen, der Ester der Acrylsäure und Methacrylsäure mit verzweigten und unverzweigten Alkoholen mit 1 bis 12 C-Atomen, Vinylaromaten, Vinylhalogenide, Diene und alpha-Olefine, in Gegenwart von Polyvinylalkohol und gegebenenfalls Trocknung der damit erhältlichen Dispersion, dadurch gekennzeichnet, da? nach Abschluß der Polymerisation zu der Dispersion 0.3 bis 3.0 Gew.-%, bezogen auf das Gesamtgewicht der Dispersion, ein oder mehrere Emulgatoren aus der Gruppe der anionischen, kationischen und nichtionischen Emulgatoren zugegeben werden.

WO 01/18143 A1

DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

Atty. Docket No. WAS0513PUSA
First Named Inventor Thomas Kohler et al

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PROCESS FOR PREPARING ADHESIVES HAVING IMPROVED ADHESION

the specification of which:

[ ] is attached hereto; or

[X] was filed on (MM/DD/YYYY) September 7, 2000 as U.S. Application Number or PCT International Application Number PCT/EP00/08753, and was amended on (MM/DD/YYYY) ___ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below, and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	*Country*	*Foreign Priority Date (MM/DD/YYYY)*	*Priority Not Claimed*	*Certified Copy Attached? (Yes/No)*
199 43 104.3	Germany	September 9, 1999		

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

Application Number(s)	*Filing Date (MM/DD/YYYY)*

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application.

Application Number(s)	*Filing Date (MM/DD/YYYY)*	*Status: Patented, Pending, Abandoned*

Declaration for Patent Application (cont'd.) Atty. Docket No. WAS0513PUSA

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41

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

10

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